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Environmental controls on the stable isotopic composition of *Mercenaria mercenaria*: Potential application to paleoenvironmental studies

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[1] We have investigated the environmental controls of seasonally resolved records of oxygen and carbon isotopes of modern *Mercenaria mercenaria* bivalves collected live from five coastal sites along the east coast of North America. Seasonal profiles of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ obtained by subsampling the incremental growth layers of aragonite were compared with in situ historical records of temperature and salinity. We show that *M. mercenaria* $\delta^{18}\text{O}$ profiles track accurately the seasonal variations of water temperature and that variations in growth rates do not affect the shell $\delta^{18}\text{O}$ values. Growth rates are strongly reduced or interrupted below water temperatures ranging from 8 to 10°C, implying that only bivalves sampled in tropical areas track the full amplitude of seasonal variations. Although further measurements of water $\delta^{18}\text{O}$ and a better understanding of seasonal variations of the water $\delta^{18}\text{O}$ -salinity relationships are necessary, *Mercenaria mercenaria* bivalves appear to precipitate their shell close to isotopic equilibrium. Whereas the amplitude of the seasonal profiles of $\delta^{18}\text{O}$ reflects variations in water temperature, the annual average $\delta^{18}\text{O}$ decreases with latitude, reflecting the trend of rainfall and riverwater $\delta^{18}\text{O}$ with latitude over the Northern American continent.

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1. Introduction

[2] Mollusks secrete shells composed of successive daily layers of calcium carbonate. The interaction between the environment and the bivalve's physiology controls most of the features of the shell's growth patterns and geochemical composition. Numerous studies have thus aimed to use the growth increments of marine bivalves to obtain information on the waters in which the shells grew with seasonal resolution [e.g., Aharon and Chappell, 1986; Andreasson and Schmitz, 1998; Bemis and Geary, 1996; Cohen and Tyson, 1995; Jones, 1980; Killingley and Berger, 1979; Weidman and Jones, 1994]. Marine mollusks are distributed in various ecological niches, from shallow coastal to deeper sublittoral waters, over large latitudinal ranges from the tropics to high latitudes. More importantly they commonly precipitate their shell in or close to isotopic equilibrium with the water in which they grew [e.g., Aharon and Chappell, 1986]. Mollusks thus offer unique possibilities to reconstruct past changes of environmental parameters, such as temperature (T), salinity (S) and productivity, at low and high latitudes with seasonal resolutions.

[3] This study investigates the environmental control on the oxygen ($\delta^{18}\text{O}_s$, s for shell) and carbon ($\delta^{13}\text{C}_s$) isotopic composition of the modern marine mollusk *M. mercenaria*. Studies conducted on planktonic foraminifera [Bemis *et al.*, 1998], gastropods [Grossman and Ku, 1986] and corals [Leder *et al.*, 1996; Wellington *et al.*, 1996] have shown that biogenic carbonate $\delta^{18}\text{O}$ reflects a combination of both the temperature and the oxygen isotopic composition of water ($\delta^{18}\text{O}_w$) [Epstein *et al.*, 1953]. Oceanic $\delta^{18}\text{O}_w$ is highly correlated to changes in salinity reflecting local evaporation, precipitation and river runoff. The relationship between the temperature, the $\delta^{18}\text{O}_w$ and the $\delta^{18}\text{O}_s$ differ for calcite and aragonite [Epstein *et al.*, 1953; Böhm *et al.*, 2000; Grossman and Ku, 1986]. Isotopic disequilibrium related to the physiology of each organism can cause deviations from the theoretical relationships, such as is the case for corals [Weber and Woodhead, 1972]. Factors controlling biogenic carbonate $\delta^{13}\text{C}$ are more complex because of the interaction between the physical parameters, chem-

ical, and physiological processes. Thus mollusk $\delta^{13}\text{C}$ has been shown to be an indicator of upwelling activity [Killingley and Berger, 1979], productivity [Krantz *et al.*, 1987], and changes in river runoff [Rahimpour-Bonad *et al.*, 1997; Surge *et al.*, 2001]. Finally, changes in metabolic activity and growth rates can control mollusk $\delta^{13}\text{C}$, in particular when there is significant incorporation of respiratory CO_2 [Klein *et al.*, 1996].

[4] *M. mercenaria* is a coastal aragonitic infaunal bivalve which lives in the intertidal and shallow subtidal zones and can be found in sheltered coves and bays often close to large estuaries, from the Gulf of Mexico to the Gulf of St. Lawrence along the eastern coast of North America [Harte, 2001]. These areas correspond to the physical border between open-ocean and continental zones and are characterized by highly variable water hydrography. Strong gradients in water properties such as salinity, trace elements and productivity, as well as large seasonal variations in water temperature, can be observed in the coastal zones. Coastal marine bivalves could potentially provide unique information on past environmental variability with seasonal resolution within highly sensitive and variable coastal areas. To better constrain the significance of stable isotope profiles reconstructed from fossil *M. mercenaria* we conducted a calibration study using specimens collected live from five coastal sites along a north-south transect of the eastern coast of the North America. Our goal has been to investigate the environmental controls on $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$, and to evaluate the potential use of *M. mercenaria* in paleoenvironmental studies. We obtained monthly resolved profiles of $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$ by subsampling the annual growth layers of aragonite secreted by *M. mercenaria*, which we compared with the historical instrumental records of the water T and S in which they grew.

2. Material, Methods, and Hydrographic Data

2.1. Description of Calibration Sites and Hydrographic Data

[5] We obtained live *M. mercenaria* samples, harvested at known dates, from five sites along the

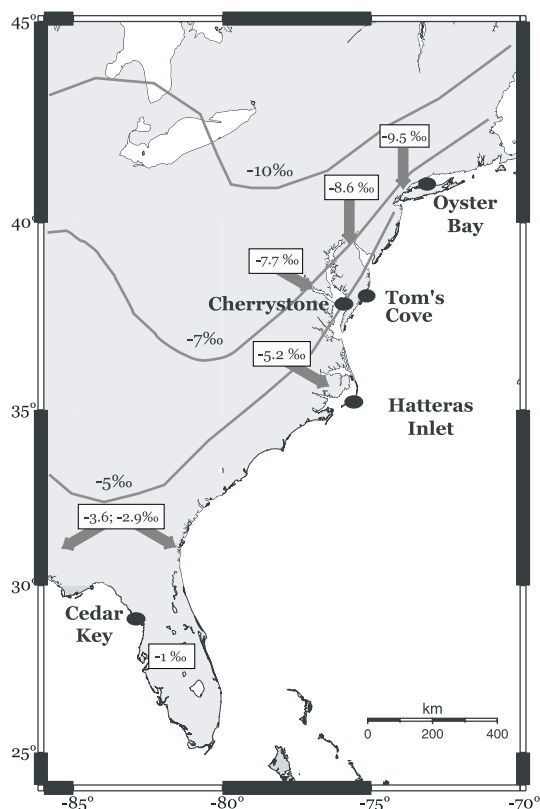


Figure 1. Map showing location of sampling sites (solid back circles) of modern *M. mercenaria* presented in this study. Average $\delta^{18}\text{O}_w$ values of local rivers are indicated in boxes and are from Coplen and Kendall [2000]. Precipitation $\delta^{18}\text{O}$ contours (solid gray lines) are from Fairbanks [1982].

eastern coast of the United States from 28°N to 42°N at water depth ranging from 2 to 5 meters (Figure 1, Table 1). These sites were chosen in order to obtain bivalves which had grown in

different average water T and S, with different seasonal ranges.

[6] Five shells were cultured and harvested in local aquacultures where T and S of bottom waters were monitored regularly with average weekly to bi-monthly time resolution (Figure 2 and Table 1). Cedar Key (CK) is located in northern Florida on the Gulf of Mexico 15 km south of the mouth of the Suwannee River. A modern shell was sampled close to 2 monitoring sites where T and S were measured with weekly resolution. Average T and S for these sites range from 10 to 32°C and average S from 11 to 30 psu. Tom's Cove site, where shells TC1 and TC2, were sampled is located in a sheltered cove on the eastern side of the Delmarva Peninsula at the southern tip of Assateague Island and is distant from any major river discharge area. The S is high, 28 to 34 psu, and water T ranges from 2 to 28°C. Shell CH, was sampled at Cherrystone which is located on the western side of the Delmarva Peninsula, at a similar latitude as Tom's Cove, but on the Chesapeake Bay. The annual T range is thus similar, from 1 to 29°C but S is lower, from 20 to 27 psu. Shell OB was sampled at Oyster Bay which is the northernmost site, located on the northern side of Long Island east of New York City. Annual T ranges from 1 to 24°C and S from 24 to 28 psu.

[7] The shell collected at Hatteras Inlet (HI) was not cultured in a shellfish farm. T and S were measured approximately 7 km from the shell-

Table 1. Description of Sample Material, Including Sampling Location, Shell Name, Approximate Age of Shell Estimated From Number of Dark/Light Increments, Average and Range of Water Temperature, and Average and Range of Salinity

| Sampling Site | Shell Name ^a | S, T Data | Shell Age, years | Mean T, °C | T (Min–Max) | Mean S, psu | S (Min–Max) |
|---------------------|-------------------------|-----------|------------------|------------|-------------|-------------|-------------|
| Oyster Bay (NY) | OB(10/2000) | 1998–2000 | ~3 | 14.5 | 1–24 | 26 | 24–28 |
| Tom's Cove -1 (MD) | TC(10/2000)-1 (TC1) | 1991–1999 | ~5 | 16.4 | 2–28 | 31 | 28–34 |
| Tom's Cove -2 (MD) | TC(10/2000)-2 (TC2) | – | ~6 | 16.4 | 2–28 | 31 | 28–34 |
| Cherrystone (MD) | CH(10/2000) | 1999–2000 | ~2 | 17.7 | 1–29 | 23 | 20–27 |
| Hatteras Inlet (NC) | HI(08/1999) | 1990–2000 | ~12 | 18.5 | 4–29 | 24 | 15–30 |
| Cedar Key (FL) | CK(06/1999) | 1990–1999 | ~4 | 22 | 10–32 | 24 | 11–30 |

^a Initials of the sampling location and month/year of sampling.

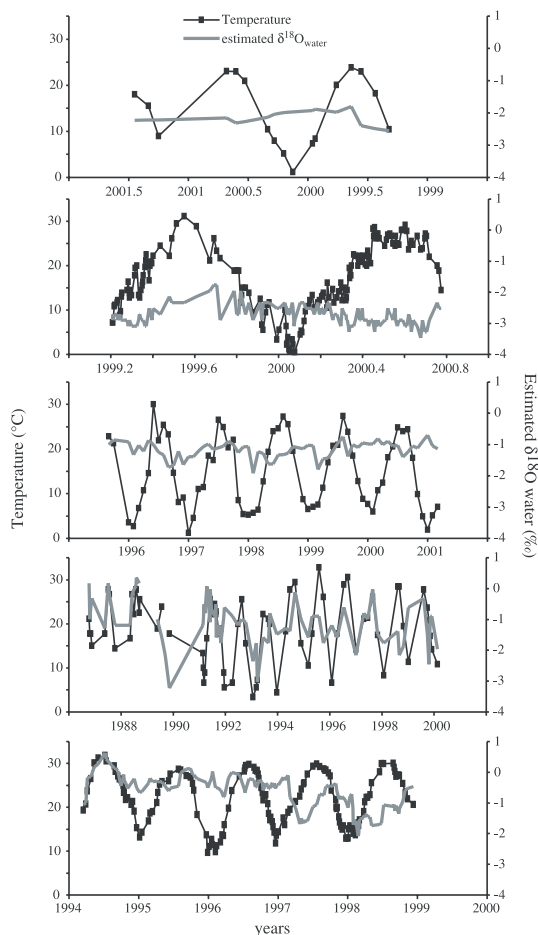


Figure 2. Water temperature and estimated $\delta^{18}\text{O}_w$ data for each sampling site. $\delta^{18}\text{O}_w$ were estimated using local $\delta^{18}\text{O}_w$ /salinity relationships given in Table 2.

sampling site on average every 2 months since 1987. Large salinity variations are observed at this site due to its location at the boundary between the Palmico Sound and the open North Atlantic Ocean,

but also because T and S were measured from surface and not bottom waters.

2.2. Constraints on $\delta^{18}\text{O}_w$ and the $\delta^{18}\text{O}_w$ -S Relationships

[8] We estimated the $\delta^{18}\text{O}_w$ from the salinity measurements using the local average $\delta^{18}\text{O}_w$ -S relationships (Table 2, Figure 2). *M. mercenaria* lives in coastal tidal to subtidal areas in water depths of up to 12 meters [Harte, 2001]. Such areas are subject to large intraannual variations of S, owing to mixing of local rainfall and river runoff with ocean waters. Rainfall and river water $\delta^{18}\text{O}_w$ across the North American continent decrease northward and inland reflecting the distillation processes that affect water vapor as it migrates poleward [Dansgaard, 1964] (Figure 1). Significant seasonal $\delta^{18}\text{O}_w$ variations have been observed in river water of eastern North America with summer-fall water up to 2‰ more positive than winter-spring water [Fairbanks, 1982]. For example, the amplitude of the seasonal variations of $\delta^{18}\text{O}_w$ in the Susquehanna River, one of the major tributaries feeding the Chesapeake Bay, is around 3‰ [Coplen and Kendall, 2000; Kendall and Coplen, 2001]. The $\delta^{18}\text{O}_w$ /S relationships in these coastal environments reflect the mixing of river runoff and oceanic waters.

2.3. Sampling Technique

[9] The shells were cut along their maximum growth axis, from the umbo to the ventral margin using a water-cooled diamond saw. Sections of the shells were mounted on petrographic slides, ground

Table 2. The $\delta^{18}\text{O}_w$ -S Relationships for Each Sampling Site and the Salinity Range for Which These Relationships Have Been Defined

| Sampling Site | Average Rain $\delta^{18}\text{O}_w$, ‰ | Average River $\delta^{18}\text{O}_w$, ‰ | $\delta^{18}\text{O}_w$ /S Relationships ^a |
|----------------|---|--|--|
| Oyster Bay | -6 | -9.5 (Hudson) | $\delta^{18}\text{O}_w = 0.16 S - 6.31$ (1) |
| Tom's Cove | -5 | -8.8 (Delaware) | $\delta^{18}\text{O}_w = 0.19 S - 7.08$ (2) |
| Cherrystone | -5 | -8.5 (Susquehanna) | $\delta^{18}\text{O}_w = 0.19 S - 7.08$ (2) |
| Hatteras Inlet | -5 | -5.2 (Tar) | $\delta^{18}\text{O}_w = 0.17 S - 5.19$ (3) |
| Cedar Key | -0.5 | -1 (Lithia) | $\delta^{18}\text{O}_w = 0.12 S - 3.39$ (4) |

^a The $\delta^{18}\text{O}_w$ -S relationships are from (1) R. G. Fairbanks (personal communication, 2001) (see Figure 8), (2) Khim and Krantz [1996], who did a hydrographic survey conducted on the inner shelf between 10 and 20 meters water depth, from southern Delaware Bay to the mouth of the Chesapeake Bay, (3) estimated assuming a linear mixture between a river water end-member, taken from Coplen and Kendall [2000] and an ocean end-member taken from GISS database (G. A. Schmidt et al., Global seawater oxygen-18 database, <http://www.giss.nasa.gov/data/o18data/>, 1999), and (4) Yobbi [1992] conducted a hydrographic survey 36 km south of the Cedar Key site.

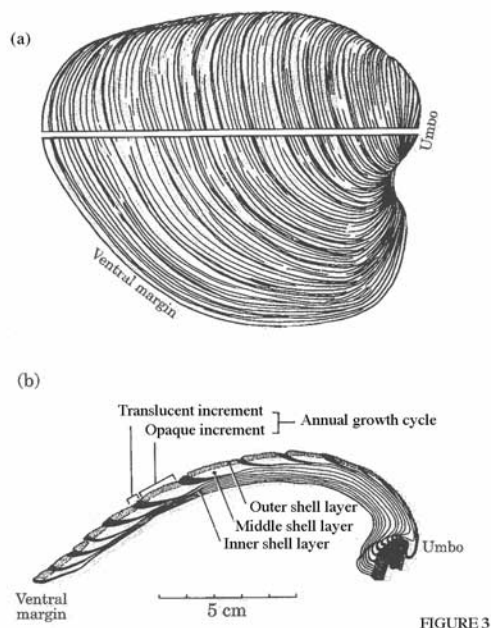


Figure 3. Drawing of *M. mercenaria* shells from Quitmyer et al. [1997]. a) Exterior surface of left valve and position of the maximum growth section. b) Internal growth increments and shell layers.

down to approximately 1mm thickness and polished for easier viewing of the growth increments. Cross sections of *M. mercenaria* shells reveal three successive layers of aragonite: the outer shell layer (also called the outer prismatic layer), the middle shell layer where the annual growth increments are largest and can be easily viewed, and the inner shell layer where the annual bands are closely superimposed (Figure 3). Alternating dark (translucent) and light (opaque) macroscopic increments were clearly visible within the middle layer [Jones, 1980; Quitmyer et al., 1997]. The periodicity of growth bands of marine bivalves range from semi-diurnal to annual and result from the interaction of the environment and the physiology of each species [Lutz and Rhoads, 1980]. Jones and Quitmyer [1996] showed that water temperature was the major factor controlling the dark/light incremental growth in *M. mercenaria*. These authors also observed a transition whereby dark increments are formed in the summer-fall from Florida to Georgia whereas they are formed in the winter farther north in Rhode Island. See Fritz [2001, and references therein] for further details on the shell structure of *M. mercenaria*.

[10] We subsampled the annual growth layers within the middle layer using a high-precision Micromill device consisting of a dental drill mounted under a binocular microscope. The shells are mounted on a fixed three-axis computer-controlled micro-positioning stage. Magnified sections of the shell can be viewed on screen via a video camera mounted on the microscope. Successive drill lines parallel to the growth increments are defined on the screen, along which samples of carbonate are extracted. This apparatus enables the drill to accurately sample growth increments with a precision of $\pm 10 \mu\text{m}$, avoiding mixing layers of carbonate of different age and mixing between the outer, middle and inner layers. We were able to obtain samples of carbonate powder with weekly to monthly resolution, depending on the growth rate of the bivalves. The average spacing of samples is between 250 and 400 μm .

2.4. Stable Isotope Analyses

[11] The powdered carbonate samples received no additional thermal or chemical pre-treatment before being dissolved in 100% H_3PO_4 at 90°C in a MultiPrep sample preparation device. The resulting CO_2 gas was analyzed using a Micromass Optima mass spectrometer at the University at Albany, State University of New York. Approximately 10% of the samples were analyzed in duplicate. The average difference between duplicate analyses of the same sample ($n = 48$) was 0.08‰ for $\delta^{18}\text{O}_\text{s}$ and 0.05‰ for $\delta^{13}\text{C}_\text{s}$. The standard deviation of 88 samples of international reference NBS-19, interspersed among the bivalve samples in daily runs and analyzed over a 2-year period, was better than 0.04‰ for $\delta^{18}\text{O}_\text{s}$ and 0.02‰ for $\delta^{13}\text{C}_\text{s}$, identical to the precisions attained for NBS-19 during the entire six years the University at Albany mass spectrometry laboratory has been in operation. All data are reported relative to Vienna Pee Dee belemnite (VPDB).

3. Results

3.1. Records of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

[12] Profiles of $\delta^{18}\text{O}_\text{s}$ and $\delta^{13}\text{C}_\text{s}$ are plotted as a function of shell height in Figure 4. Calcium

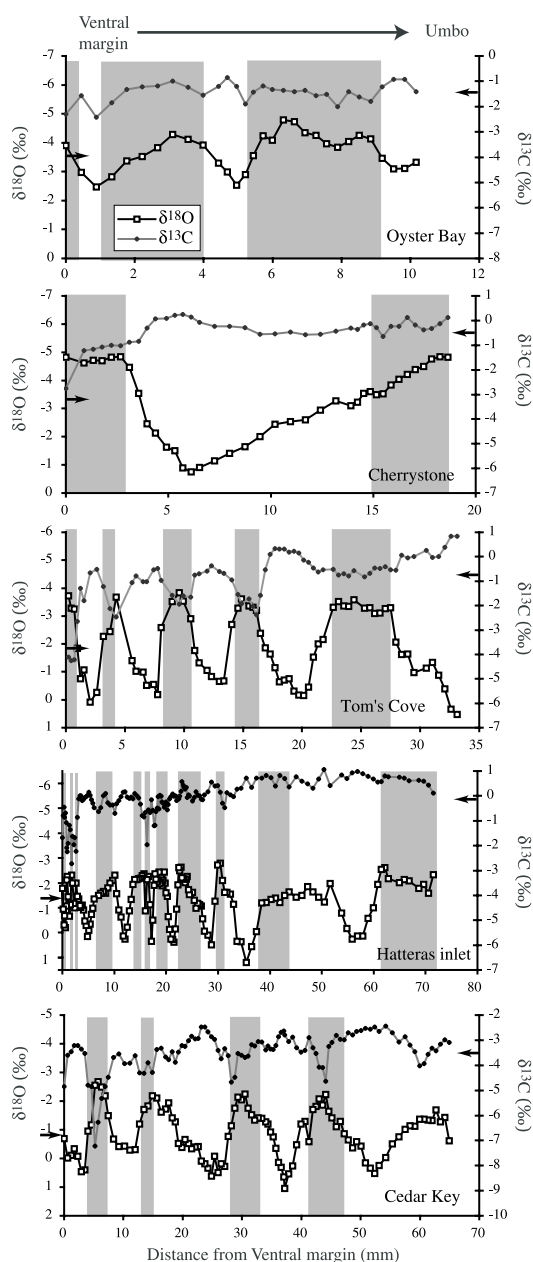


Figure 4. The $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$ records versus distance from ventral margin of the shell. Note that the $\delta^{18}\text{O}_s$ axis has been inverted. The gray bands correspond to the position of the dark-summer (labeled “translucent” in Figure 3) macroscopic increments which alternate with light-winter (labeled “opaque” in Figure 3) macroscopic increments. Arrows at vertical axes indicate average $\delta^{18}\text{O}_s$ (−3.7‰: OB, −3.2‰: CH, −1.9‰: TC1, −1.3‰: HI, −0.9‰: CK) and average $\delta^{13}\text{C}_s$ (−1.4‰: OB, −0.4‰: CH, −0.9‰: TC1, −0.1‰: HI, −3.5‰: CK).

carbonate powders drilled from the edge of the ventral margin were secreted most recently, whereas material drilled closer to the umbo was secreted during the earlier phase of life. All $\delta^{18}\text{O}_s$ records yield seasonal oscillations where the more negative values coincide with the position of the summer dark increments and the more positive values coincide with the winter light increments (Figure 4). The first samples, at the edge of the ventral margin, are all obtained within a summer dark layer except for the Cedar Key sample. CK is the only shell to have been harvested in early June, the others were sampled in late summer to fall period (Table 1). This observation differs from previous results which showed that the light layer was secreted in summer in the northern latitudes [Jones and Quitmyer, 1996]. Our $\delta^{18}\text{O}_s$ records generally agree with previously published $\delta^{18}\text{O}_s$ records of modern *M. mercenaria* [Quitmyer et al., 1997] except the Oyster Bay record in which summer and winter $\delta^{18}\text{O}_s$ is approximately 1‰ more negative than that of a shell from Narragansett Bay, Rhode Island [Jones and Quitmyer, 1996].

[13] The average $\delta^{18}\text{O}_s$ values, as well as the winter and the summer $\delta^{18}\text{O}_s$ values decrease with increasing latitude (Figure 4) which is contrary to what would be expected if T was the major factor controlling the $\delta^{18}\text{O}_s$. The most positive average $\delta^{18}\text{O}_s$ (−0.9‰) is recorded at Cedar Key, while the most negative average $\delta^{18}\text{O}_s$ (−3.7‰) is recorded in Oyster Bay.

[14] The average $\delta^{13}\text{C}_s$ values range from −0.1‰ in Hatteras Inlet to −3.5‰ in Cedar Key (Figure 4). The $\delta^{13}\text{C}_s$ records do not show any latitudinal trends and no seasonal oscillations as is observed for $\delta^{18}\text{O}_s$ records. However, more negative $\delta^{13}\text{C}_s$ values are associated with more negative (i.e., summer) $\delta^{18}\text{O}_s$ values of TC, CK and to a lesser degree CH (Figure 4).

3.2. Reproducibility and Variations in Growth Rates

[15] We replicated measurements of $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$ on two shells of different age harvested in Tom’s Cove (TC1 and TC2), at the same water depth and on the same day to test the reproduc-

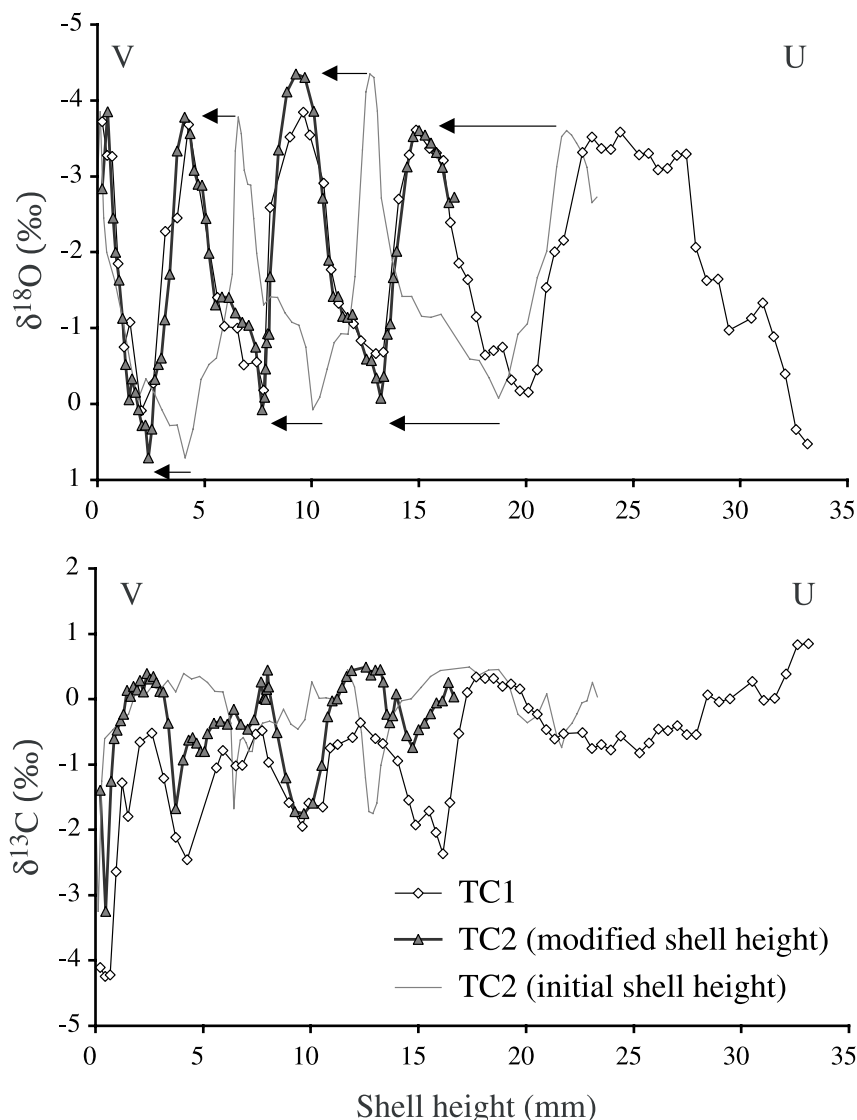


Figure 5. Comparison of $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$ profiles of shells TC1 and TC2, both harvested from the same location on the same day. The initial shell height of TC2 (gray line) has been modified: TC2 results are plotted as a function of TC1 shell height. Arrows indicate correlation tie points of TC1 and TC2 $\delta^{18}\text{O}_s$ values. v = ventral margin; u = umbo.

ibility of our measurements (Figure 5). We modified the initial shell height of TC2 using the *Analyseries* software [Paillard *et al.*, 1996], in order to accurately compare variations of $\delta^{18}\text{O}_s$ and $\delta^{13}\text{C}_s$ of each shell. We considered that the succession of each $\delta^{18}\text{O}_s$ minima (summer) and maxima (winter) corresponded to the same yearly growth and were coeval. We thus applied variable shifts throughout the series, as seen in Figure 5.

[16] The thickness of the light and dark increments of shell TC1 are similar suggesting that this shell

has a rather constant growth rate throughout the winter and summer seasons. Conversely, shell TC2 has large light-winter incremental layers (high $\delta^{18}\text{O}_s$) and thin dark-summer layers (low $\delta^{18}\text{O}_s$) indicating that growth rates for this specimen appear higher in winter than in summer. The comparison of TC1 and TC2 suggests that yearly growth rates can be significantly variable within a given mollusk population which experienced similar environmental constraints. This observation challenges the general assumption that bivalves grow more rapidly in summer versus winter. *Griz-*



zle *et al.* [2001] showed that *M. mercenaria* has an optimal temperature of growth, between 20°C and 24°C, but that there was significant variations in growth rates within a given population in agreement with these results.

[17] The comparison of the $\delta^{18}\text{O}_s$ profiles of TC1 and TC2 shows that the $\delta^{18}\text{O}_s$ can be reproduced faithfully in great detail (Figure 5). Only one significant difference ($\sim 0.5\text{‰}$) is observed at 10 mm shell height and could easily be explained by different temporal resolution. Although the growth rates of TC1 and TC2 were different, particularly during the summer periods, the $\delta^{18}\text{O}_s$ are similar suggesting that the $\delta^{18}\text{O}_s$ of *M. mercenaria* do not appear to be affected by differences in growth rates (Figure 5).

[18] The $\delta^{13}\text{C}_s$ have similar trends, both records show more negative $\delta^{13}\text{C}_s$ associated with more negative summer $\delta^{18}\text{O}_s$ values. Similarly the $\delta^{13}\text{C}_s$ values closest to the ventral margin, the most recently secreted carbonate layers, are significantly more negative when compared to the earlier phase of life. However, in contrast with the $\delta^{18}\text{O}_s$ profiles, the $\delta^{13}\text{C}_s$ records show pronounced offsets, by as much as 2‰.

3.3. Seasonal Trends of $\delta^{18}\text{O}_s$

[19] The amplitude of the seasonal $\delta^{18}\text{O}_s$ increases from 3.7‰ in Cedar Key to 4.6‰ in Tom's Cove, and then decreases to 2.3‰ in Oyster Bay. The shell from Hatteras Inlet is the longest-lived bivalve; its seasonal $\delta^{18}\text{O}_s$ amplitude gradually decreases, probably due to a decrease in growth rates with age. Seasonal trends of mollusk $\delta^{18}\text{O}$ records have been shown to reflect either the local seasonal variations of T [Khim *et al.*, 2000; Krantz *et al.*, 1988] or of S [Ingram *et al.*, 1996] depending on environmental settings. Using the local $\delta^{18}\text{O}_w$ -S relationships (Table 2) and assuming no seasonal variations of these relationships, we estimated the average seasonal range of $\delta^{18}\text{O}_w$ (Figure 2). At Tom's Cove, for example, the maximum annual $\delta^{18}\text{O}_w$ range is 1.1‰, which is smaller than the observed $\delta^{18}\text{O}_s$ seasonal amplitude of 4.3‰. Furthermore, despite considerable annual variability, the salinity records do not exhibit a

clear seasonal variation at each site (Figure 2). The more negative $\delta^{18}\text{O}_w$ observed at Cedar Key and Hatteras Inlet are associated with lowest S values, <15 psu and are rare events most probably related to episodic dramatic increases in rainfall and river runoff. These observations demonstrate that the seasonal trends of *M. mercenaria* $\delta^{18}\text{O}_s$ mainly reflect seasonal oscillations of water T.

4. Discussion

4.1. Oxygen Isotope

4.1.1. Comparison of Measured and Predicted $\delta^{18}\text{O}$

[20] In this section we compare predicted values of carbonate $\delta^{18}\text{O}_{\text{pred}}$ ("pred" for predicted) derived from the local T and S data with the measured aragonite $\delta^{18}\text{O}_s$. We chose to use the equation given by Böhm *et al.* [2000] (equation (1)), which includes data from coralline sponges, bivalve and foraminifera data [Grossman and Ku, 1986], gastropode data [Rahimpour-Bonad *et al.*, 1997] and inorganic aragonite data [Tarutani *et al.*, 1969]:

$$T = -4.42 * (\delta^{18}\text{O}_s - \delta^{18}\text{O}_w) + 20, \quad (1)$$

where $\delta^{18}\text{O}_w$ is expressed versus SMOW and $\delta^{18}\text{O}_s$ is expressed versus VPDB. This equation is defined for T ranging from 3 to 28°C and the specimens of modern *M. mercenaria* lived in T which ranged from 1 to 32°C (Table 1).

[21] Due to potential variations of seasonal growth rates and periods of growth cessation [Ansell, 1968; Harrington, 1989; Krantz *et al.*, 1987; Weidman and Jones, 1994] we first compare the $\delta^{18}\text{O}_{\text{pred}}$ and the $\delta^{18}\text{O}_s$ in frequency histograms ranging from -6‰ to +3‰ (Figure 6). These diagrams enable comparisons of the $\delta^{18}\text{O}_{\text{pred}}$ and $\delta^{18}\text{O}_s$ while taking into account the frequency of extreme S and T values and without attributing an age to each individual $\delta^{18}\text{O}_s$ measurement.

[22] The average values and the distributions of the $\delta^{18}\text{O}_s$ and the $\delta^{18}\text{O}_{\text{pred}}$ are in good agreement for the Cedar Key and Hatteras Inlet shells (Figure 6). The $\delta^{18}\text{O}_{\text{pred}}$ are distributed over a wider range than the $\delta^{18}\text{O}_s$, which could result from differences

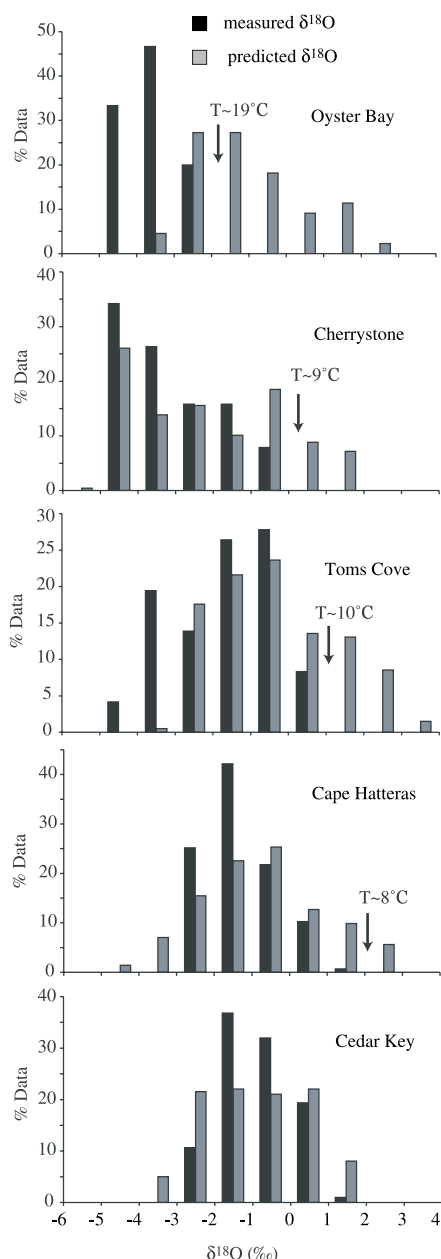


Figure 6. Histogram frequency diagrams showing the range and probability of obtaining given values of $\delta^{18}\text{O}_{\text{pred}}$ (gray columns) estimated from local T and S historical records (that overlapped the age of the bivalves at each location), compared to the measured $\delta^{18}\text{O}_s$ (dark columns). Vertical arrows indicate estimated temperature of growth reduction or cessation.

in the temporal resolution of the records. Each $\delta^{18}\text{O}_s$ measurement represents a mean of ~ 2 weeks to a month whereas each $\delta^{18}\text{O}_{\text{pred}}$ is derived from discrete daily measurements of T and S. Ideally we would need continual daily records of T and S

which would then be averaged over weekly to monthly periods. More significant offsets between the $\delta^{18}\text{O}_s$ and $\delta^{18}\text{O}_{\text{pred}}$ can be observed further north in Tom's Cove, Cherrystone, and Oyster Bay. The $\delta^{18}\text{O}_s$ show an overall more negative distribution when compared to the $\delta^{18}\text{O}_{\text{pred}}$. For example, there are no measured $\delta^{18}\text{O}_s$ values of shell CH above 0‰ whereas the winter $\delta^{18}\text{O}_{\text{pred}}$ reach +1 to +2‰. Also warm-summer $\delta^{18}\text{O}_s$ values of shells TC1, TC2, and OB are more negative, by 1 to 1.3‰, than $\delta^{18}\text{O}_{\text{pred}}$ implying that the shells appeared to have lived in waters 4–5°C warmer or 4.5–7psu less saline than those measured. These offsets cannot be attributed to such large errors of the T and S measurements. In the following sections we investigate the potential effects of 1) uncertainties related to seasonal changes in growth rates and periods of growth cessation and 2) uncertainties of the $\delta^{18}\text{O}_w$ -S relationships and their seasonal evolution.

4.1.2. Variations in Growth Rates and Growth Interruptions

[23] The average predicted winter temperatures corresponding to the most positive $\delta^{18}\text{O}_s$ values of HI, TC, and CH are $\sim 8^\circ\text{C}$, 10°C , 9°C , respectively (Figure 6). One explanation for the observed difference between $\delta^{18}\text{O}_s$ and $\delta^{18}\text{O}_{\text{pred}}$ could be a temperature-controlled growth cessation below these respective temperatures. Previous studies have shown that the growth of *M. mercenaria* either stopped or slowed considerably below 9–10°C [Ansell, 1968; Fritz, 2001]. This temperature range is close to the temperature of growth cessation estimated from shells CK, CH and TC. However, the estimated the temperature of growth cessation in OB is $\sim 19^\circ\text{C}$ which is considerably different from the other shells and from previous studies [Ansell, 1968; Fritz, 2001].

[24] Growth breaks in *M. mercenaria* shells are commonly marked by V-shaped notches particularly visible in the outer prismatic layer [Kennish, 1980]. When stressed, bivalves stops growing and their shells remain closed, reducing the transfer of well-oxygenated water to the inner shell. The bivalve survives by anaerobic respiration, this increases the acidity of the extrapallial fluids and



leads to dissolution of the shell [Kennish, 1980]. We found visible indications of periods of growth breaks in HI, particularly between 0 and 3 mm corresponding to the older phase of its life, and in OB (Figure 4). However, on a macroscopic level there is no visible evidence of growth cessation in shells TC1, TC2 and CH although water winter temperatures fall well below 10°C at both locations. Furthermore, shell TC2 has larger light (winter) and significantly thinner dark (summer) increments suggesting that shell TC2 grew faster during the winter relative to the summer season (Figure 5). Such an observation contradicts the existence of a winter growth interruption. One explanation could be that shell TC2 has a highly variable annual growth rates, with minimum in winter and maximum during spring and fall seasons.

[25] Overall, our results suggest that either extremely reduced growth rates or growth cessation occurred below water temperatures ranging from 8–10°C, explaining the observed isotopic offsets between winter $\delta^{18}\text{O}_s$ and $\delta^{18}\text{O}_{\text{pred}}$ of TC1, TC2, CH and perhaps HI. The absence of any visible notch in TC1, TC2 or CH could be explained by a gradual decrease in winter growth rates. Further studies and more detailed observations of the shell structures would be necessary.

[26] The estimated temperature at which growth is interrupted or strongly reduced at Oyster Bay is exceptionally high, ~19°C. This could reflect the length of the winter season, with water temperatures remaining below 10°C longer in the northern versus the southern sites. Perhaps longer winters inhibited the capacity of these bivalves to rapidly resume growth. The long winter season could also have forced the shell sampled in Oyster Bay to remain in an anaerobic situation for a longer period leading to partial dissolution of the shell. Food availability or other local environmental factors could also play an important role. These effects combined could account for the high apparent temperature of growth cessation estimated for OB. We must acknowledge the 1‰ difference between the $\delta^{18}\text{O}_s$ values of the Oyster Bay shell and the previously published record from Narragansett Bay [Jones and Quitmyer, 1996], more data

from this site will be needed to confirm this result. Finally, Ansell [1968] and Fritz [2001] also observed a temperature-controlled growth reduction in summer, at 30–31°C. The *M. mercenaria* shells that we have studied lived in waters that rarely rise above 30°C (Table 1), and we cannot accurately confirm this observation.

4.1.3. Age Models

[27] We used the estimated temperature of growth cessation to express the $\delta^{18}\text{O}_s$ data versus age which we then compare to the $\delta^{18}\text{O}_{\text{pred}}$ on an age scale (Figure 7). Age models for each shell were constructed assuming that the seasonal profiles of $\delta^{18}\text{O}_s$ were correlated to the seasonal variations of water T and by assuming that the most positive values of $\delta^{18}\text{O}_s$ were secreted at the estimated temperature of growth cessation for each shell. This representation illustrates how the shell from CK reproduces the full range of seasonal variability whereas shell OB, for example, only records the summers (Figure 7). The $\delta^{18}\text{O}_s$ records of CK and CH match closely the $\delta^{18}\text{O}_{\text{pred}}$. The comparison of the predicted and measured $\delta^{18}\text{O}$ at HI show some discrepancy which is probably related to the low resolution of hydrographic data (Figure 2), most probably enhanced by the fact that T and S were, for this location, measured in the surface instead of the bottom waters.

4.1.4. Uncertainties of the $\delta^{18}\text{O}_w$ /Salinity Relationship

[28] Offsets between the summer $\delta^{18}\text{O}_s$ and the summer $\delta^{18}\text{O}_{\text{pred}}$ of ~1‰ are observed for TC and OB (Figure 7). These differences between theoretical and measured $\delta^{18}\text{O}$ cannot be explained by growth interruptions and errors of the T and S measurements. We conducted X-ray diffraction measurements of powdered samples of shell TC2, which revealed pure aragonite and gave no evidence for mineralogical transformation. In the following section, we investigate the role of potential seasonal variations of the $\delta^{18}\text{O}_w$ -S relationships to explain the differences between $\delta^{18}\text{O}_{\text{pred}}$ and $\delta^{18}\text{O}_s$ (Figure 7). In order to quantify potential errors related to uncertainties of the estimated $\delta^{18}\text{O}_w$, we calculated the theoretical water $\delta^{18}\text{O}_w^b$

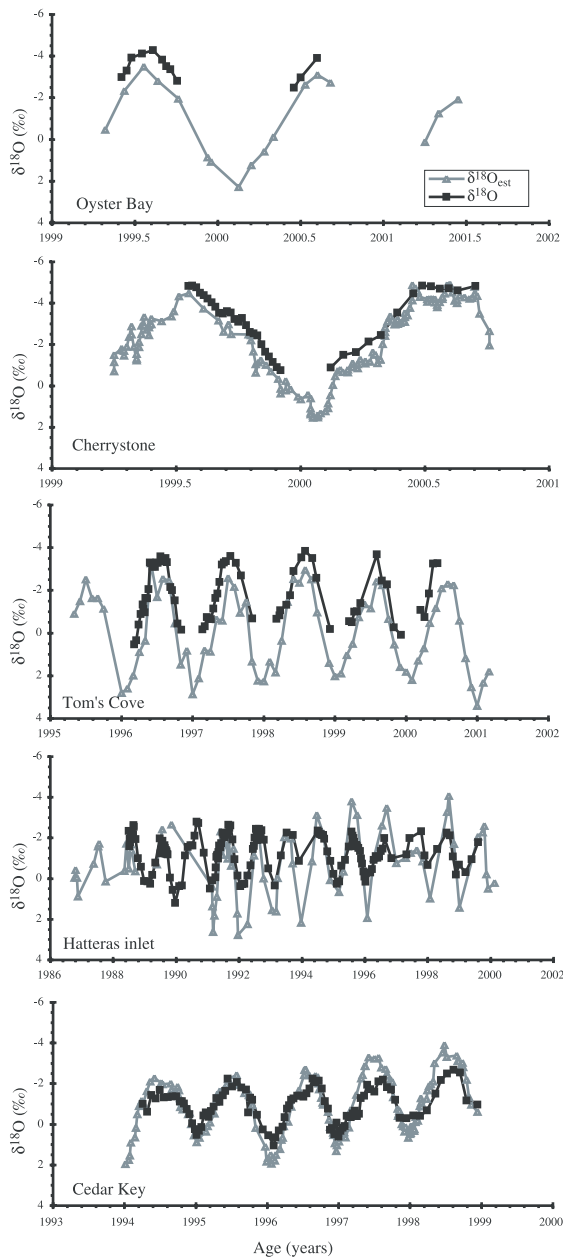


Figure 7. Comparison of $\delta^{18}\text{O}_s$ and $\delta^{18}\text{O}_{\text{pred}}$ expressed as a function of age for each location. We considered that growth cessation occurred below 19°C, 10°C, 9°C for shells OB, TC1 and CH. Due to the low temporal resolution of the hydrographic data at Hatteras Inlet, we did not attempt to consider a growth cessation below 8°C at this site. We applied a 3 point running average of the $\delta^{18}\text{O}_{\text{pred}}$ for CK and CH since the hydrographic data from these sites was obtained with higher weekly to daily temporal resolutions.

(“b” for Böhm) assuming the *Böhm et al.* [2000] equation was correct. The $\delta^{18}\text{O}_w^b$ was calculated from equation 1 using the measured most negative (summer) $\delta^{18}\text{O}_s$ values and the assigned summer temperature of growth (Figure 2). We estimated the theoretical range of $\delta^{18}\text{O}_w$ -S relationships at each site by using available freshwater and oceanic $\delta^{18}\text{O}_w$ measurements (Figure 8). Seasonal variations of the riverwater $\delta^{18}\text{O}_w$ are derived from a

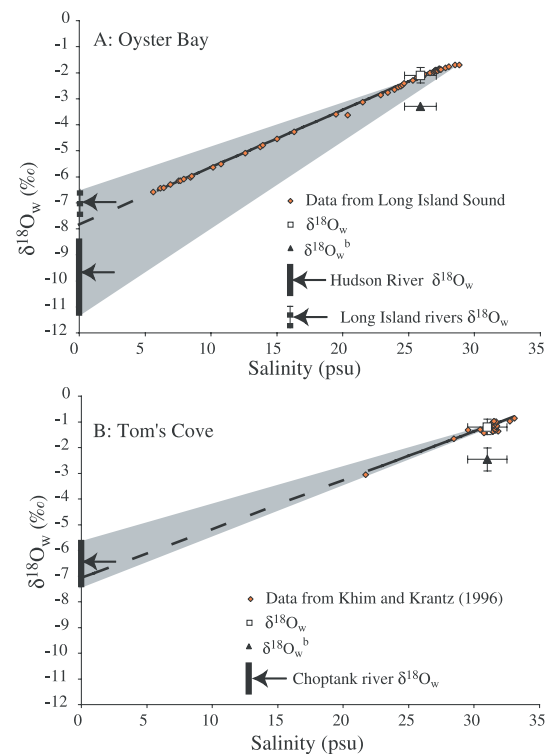


Figure 8. Comparison of the calculated $\delta^{18}\text{O}_w^b$ estimated using equation (1) [*Böhm et al.*, 2000] and the $\delta^{18}\text{O}_w$ values calculated from the local average $\delta^{18}\text{O}_w$ -S relationships (Table 2). Average $\delta^{18}\text{O}_w$ -S relationships are reported in Table 2, the solid black line indicates the range of salinity for which the $\delta^{18}\text{O}_w$ -S relationship was defined and the intersect between the abscise and the dotted line represents the theoretical freshwater end-member. The measured seasonal range of river water $\delta^{18}\text{O}_w$ is indicated by the black boxes on the left axis were taken from *Coplen and Kendall* [2000]. Arrows at vertical axes indicate average $\delta^{18}\text{O}_w$. The gray shaded area corresponds to the theoretical seasonal variability of the water $\delta^{18}\text{O}_w$ -S values. A) Comparison of summer $\delta^{18}\text{O}_w$ and $\delta^{18}\text{O}_w^b$ at Oyster Bay. B) Comparison of summer $\delta^{18}\text{O}_w$ and $\delta^{18}\text{O}_w^b$ at Tom's Cove. The average $\delta^{18}\text{O}_w$ of local river water is less negative when compared to the Susquehanna River $\delta^{18}\text{O}_w$.



survey of North American rivers conducted from 1984 to 1987 [Coplen and Kendall, 2000; Kendall and Coplen, 2001]. We have no information on seasonal variability of the oceanic $\delta^{18}\text{O}_w$ end-member offshore from each of the studied sites. Available data for the marine $\delta^{18}\text{O}_w$ show on average only small seasonal variability of 0.2 to 0.3‰ (G. A. Schmidt et al., Global seawater oxygen-18 database, <http://www.giss.nasa.gov/data/o18data/>, 1999) except at high latitudes where seasonal ice formation and melt affect the $\delta^{18}\text{O}_w$ [Strain and Tan, 1993]. A strong gradient in ocean $\delta^{18}\text{O}_w$ is observed along the eastern coast of North America. North of 45°N ocean $\delta^{18}\text{O}_w$ are <−1.5‰ whereas south of 40°N values become more positive >0.5‰ to 1‰ in the tropical zone (G. A. Schmidt et al., Global seawater oxygen-18 database, <http://www.giss.nasa.gov/data/o18data/>, 1999). Seasonal variations in the intensity of the coastal currents will thus affect the oceanic $\delta^{18}\text{O}_w$.

[29] We account for potential seasonal variability of the $\delta^{18}\text{O}_w$ -S relationship at each location by indicating the seasonal range of river water $\delta^{18}\text{O}_w$ values taken from Coplen and Kendall [2000]. The gray shaded areas in Figure 8 correspond to theoretical values of $\delta^{18}\text{O}_w$ when accounting for the seasonal variability of local river $\delta^{18}\text{O}_w$. We were thus able to compare the $\delta^{18}\text{O}_w^b$ values with the $\delta^{18}\text{O}_w$ values derived from the $\delta^{18}\text{O}_w$ -S relationships given in Table 2. $\delta^{18}\text{O}_w^b$ which fall outside the shaded areas (Figure 8) would have to be explained by variations in the ocean $\delta^{18}\text{O}_w$ end-member or would indicate that the difference between $\delta^{18}\text{O}_{\text{pred}}$ and $\delta^{18}\text{O}_s$ cannot be adequately explained by seasonal variations of the $\delta^{18}\text{O}_w$ -S relationship. At the OB site for example (Figure 8a) if the $\delta^{18}\text{O}_{\text{pred}}/\delta^{18}\text{O}_s$ difference was explained solely by a shift in the freshwater $\delta^{18}\text{O}_w$ end-member, summer $\delta^{18}\text{O}_w$ would have to be more negative, with values around −18‰. Variations in local river outflow cannot explain the observed difference since the most negative $\delta^{18}\text{O}_w$ values are around −7‰ for Long Island rivers and −11.5‰ for the Hudson and the Connecticut rivers [Coplen and Kendall, 2000]. The $\delta^{18}\text{O}_{\text{pred}}/\delta^{18}\text{O}_s$ offset observed at OB has to be explained by a ∼−1‰ negative shift in the

oceanic $\delta^{18}\text{O}_w$ end-member which is much higher than the average seasonal variability of 0.2 to 0.3‰ reported by G. A. Schmidt et al. (Global seawater oxygen-18 database, <http://www.giss.nasa.gov/data/o18data/>, 1999). Given the northern location of Oyster Bay it is possible that the southward migration of surface water with more negative $\delta^{18}\text{O}_w$ would have affected the $\delta^{18}\text{O}_w$ -S relationships at this site.

[30] Shells from TC grew in the most saline environment, with an average water salinity of 31‰ (Figure 1, Table 1). Large variations of river runoff are less likely to cause significant variations of $\delta^{18}\text{O}_w$ at this site. A shift of approximately −1‰ of the ocean $\delta^{18}\text{O}_w$ end-member toward more negative values would also be necessary to explain the $\delta^{18}\text{O}_{\text{pred}}/\delta^{18}\text{O}_s$ difference at Tom's Cove. However, when compared to the global $\delta^{18}\text{O}_w$ -S database (G. A. Schmidt et al., Global seawater oxygen-18 database, <http://www.giss.nasa.gov/data/o18data/>, 1999) it is unlikely that surface waters with such negative $\delta^{18}\text{O}_w$ values would have migrated from north of 45°N to Tom's Cove site unaffected by mixing with local waters. Another possible explanation is that *M. mercenaria* at this site can live sufficiently embedded in the sediments at depth affected by groundwater incursions. In such a case the specimen could have lived in waters less saline or with more negative $\delta^{18}\text{O}_w$ than the overlying bottom waters. In situ measurements of $\delta^{18}\text{O}_w$ and salinity from ocean water and interstitial water would be necessary. Overall, a better knowledge of the $\delta^{18}\text{O}_w$ -S relationships in coastal environments would be necessary to accurately compare theoretical oxygen fractionation with profiles of bivalve $\delta^{18}\text{O}_s$ at TC and OB sites.

4.2. Carbon Isotopes

[31] The $\delta^{13}\text{C}_s$ profiles do not exhibit any clear seasonal evolution analogous to the $\delta^{18}\text{O}_s$ profiles, suggesting that temperature has only a minor control on the $\delta^{13}\text{C}_s$ records (Figure 4). We plotted the $\delta^{13}\text{C}_s$ versus the $\delta^{18}\text{O}_s$ data for each site (Figure 9). All the results, except for shell OB, show a weak positive correlation between $\delta^{13}\text{C}_s$

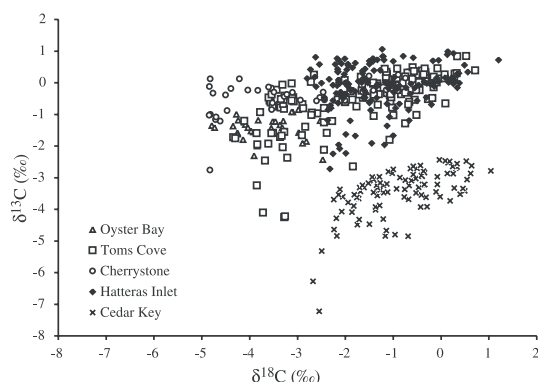


Figure 9. Plot of the carbonate $\delta^{13}\text{C}_s$ and the $\delta^{18}\text{O}_s$ of *M. mercenaria* shells. Note that the $\delta^{13}\text{C}_s$ values of CK are offset from the other results by approximately 2‰.

and $\delta^{18}\text{O}_s$, with r^2 ranging from 0.04 to 0.54 (regressions not shown in Figure 9), suggesting that kinetic effects are minimal [McConnaughey, 1989; Spero *et al.*, 1997].

[32] All $\delta^{13}\text{C}_s$ are negative ranging from 0 to -2‰ for the shells collected at the Atlantic sites and from -3 to -7‰ for CK collected on the coast of the Gulf of Mexico. Overall, these values are more negative compared to previously published bivalve $\delta^{13}\text{C}_s$ records [e.g., Krantz *et al.*, 1988; Harrington, 1989; Bemis and Geary, 1996]. These studies showed that various species of marine bivalves have $\delta^{13}\text{C}_s$ values ranging from -1 to $+2\text{‰}$ which is closer to open-ocean surface water $\delta^{13}\text{C}$ values, which are on average between $+1$ and $+2\text{‰}$ [Kroopnick, 1980]. The more negative $\delta^{13}\text{C}_s$ values recorded by *M. mercenaria* could be a consequence of their shallow water habitat close to large estuaries and reflect the input of continental runoff rich in organic matter. However, there does not appear to be any notable difference between shells sampled close to estuaries, e.g., CH, and those sampled in more saline oceanic environments, e.g., TC1 and TC2.

[33] There is an average difference of around 2‰ between the $\delta^{13}\text{C}$ of Cedar Key shell and the other shells sampled along the Atlantic Coast (Figure 9). The average $\delta^{13}\text{C}_s$ values of a modern oyster (*Crassostrea virginica*) sampled in the Blackwater River estuary in southern Florida was also very negative, between -4 and -8‰ [Surge *et al.*, 2001]. These authors suggested that the $\delta^{13}\text{C}_s$

reflected river water $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), which was very negative, from -5 to -12‰ , due to high input of organic matter [Surge *et al.*, 2001]. The offset between the $\delta^{13}\text{C}_s$ of CK and the other Atlantic shells could result from local differences in river water $\delta^{13}\text{C}_{\text{DIC}}$ but due to the lack of data we cannot test this hypothesis.

[34] The average $\delta^{13}\text{C}_s$ values of TC1 and TC2 are -0.9‰ and -0.3‰ respectively (Figure 5) illustrating the existence of small but significant intra-site variability of $\delta^{13}\text{C}_s$ as it has been observed for corals [Linsley *et al.*, 2000]. The variations of $\delta^{13}\text{C}_s$ profiles are however similar with more negative $\delta^{13}\text{C}_s$ associated with the dark-summer increments (Figure 5). Measurements of dissolved oxygen at TC and CK sites show minimum values in summer probably due to increased biological productivity and degradation of organic matter at the seafloor. Increased degradation of organic matter could account for the negative $\delta^{13}\text{C}_s$ values observed during summer at TC and CK. Similarly the difference between $\delta^{13}\text{C}_s$ of TC1 and TC2 could be explained by small differences in depth habitat. Strong gradients in pore water $\delta^{13}\text{C}$ have been observed within the initial 5 cm of sediment due to the remineralization of organic matter [McCorckle *et al.*, 1985].

[35] Finally, ontogenetic and seasonal differences in growth rates have also been shown to affect the profiles of $\delta^{13}\text{C}_s$ of marine bivalves [Klein *et al.*, 1996]. The $\delta^{13}\text{C}_s$ of HI and to a lesser degree TC1 and TC2 become more negative with increasing age. Perhaps the negative $\delta^{13}\text{C}_s$ values observed in the later phase of these bivalves lives result from a greater uptake of respiratory CO_2 due to slower growth rates with age as previously suggested by Harrington [1989].

4.3. Summary

[36] Two levels of information can be derived from *M. mercenaria* $\delta^{18}\text{O}$ profiles. The first is the water temperature: our results show that *M. mercenaria* $\delta^{18}\text{O}$ profiles track the seasonal variations of water temperature. The second is the riverwater $\delta^{18}\text{O}_w$ values: the average $\delta^{18}\text{O}$ values decrease with



increasing latitude and reflect the influence of riverwater and rain $\delta^{18}\text{O}_w$ which become more negative with increasing latitude. As previously observed for tropical bivalves [Aharon, 1991], *M. mercenaria* precipitate their shells close to isotopic equilibrium with the water in which they grew, contrarily to corals which can present offsets of up to 5‰ [e.g., Weber and Woodhead, 1972]. *M. mercenaria* reduces strongly its growth or ceases to secrete carbonate layers below water temperatures of $\sim 9\text{--}10^\circ\text{C}$. Other factors such as the length of the winter season or food availability could also influence bivalve growth at higher latitude. Small differences between theoretical and measured $\delta^{18}\text{O}$ are observed for the shells TC and OB. These differences are not explained by seasonal variations in freshwater $\delta^{18}\text{O}_w$ given by the available 1984–87 database for the North American continent [Coplen and Kendall, 2000]. Small temporal or geographical variations of the oceanic end-member are necessary to reconcile the theoretical and measured $\delta^{18}\text{O}$. This study thus illustrates how bivalve $\delta^{18}\text{O}$ records are sensitive to the high variability of coastal water hydrography in particular the $\delta^{18}\text{O}_w$ which could hamper our ability to accurately reconstruct past coastal water salinity. Additional data to constrain the geographic and seasonal variations of the $\delta^{18}\text{O}_w$ -S relationships in these areas are needed. However, the sensitivity of *M. mercenaria* $\delta^{18}\text{O}$ profiles to river water $\delta^{18}\text{O}_w$ could give rare opportunities to derive information on past coastal, river and rainfall $\delta^{18}\text{O}_w$ if supported by independent measures of temperature.

[37] *M. mercenaria* $\delta^{13}\text{C}_s$ composition reflect most probably a combination of factors ranging from the composition of $\delta^{13}\text{C}_{\text{DIC}}$, water salinity, growth rates, and depth habitat but we do not have sufficient data to test these hypothesis. Temperature appears to have little control on the $\delta^{13}\text{C}_s$ of *M. mercenaria*. The most notable difference is observed between the Florida specimen and the other bivalves collected along the Atlantic coastal sites. The more negative $\delta^{13}\text{C}_s$ of CK could reflect river runoff characterized by more negative $\delta^{13}\text{C}_{\text{DIC}}$ values but we do not have the required data to test this hypothesis.

[38] The usefulness of fossil *M. mercenaria* bivalves abundantly found in beach deposits and archeological sites along the eastern coast of North America [Quitmyer et al., 1997; Wehmiller et al., 1995] in paleoenvironmental studies will be complicated by the highly variable coastal waters $\delta^{18}\text{O}_w$. Variations in growth patterns will also hamper our ability to resolve full seasonal signals from fossil shells particularly at higher latitudes. However, full seasonal amplitude of the $\delta^{18}\text{O}_s$ could be reconstructed from fossil bivalves which grew in tropical areas and summer estimates of $\delta^{18}\text{O}_s$ could be obtained from fossil *M. mercenaria* which lived at higher latitudes. Bivalves would thus give a unique indication of past environments with seasonal resolution over a large geographic range.

5. Conclusions

[39] We show that seasonal $\delta^{18}\text{O}_s$ profiles of *M. mercenaria* reflect the seasonal variations of water temperature in which they grew. Although a better knowledge of the variations of water $\delta^{18}\text{O}_w$ are necessary *M. mercenaria* appear to precipitate their shell close to isotopic equilibrium contrarily to corals and most of the differences between theoretical and measured $\delta^{18}\text{O}$ can be explained by growth interruptions or uncertainties in the local $\delta^{18}\text{O}_w$ -S relationships. Furthermore, different summer growth rates do not appear to affect the $\delta^{18}\text{O}_s$ profiles. The $\delta^{13}\text{C}_s$ records appear more complex and are most probably controlled by a combination of environmental factors and physiological processes.

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